

Encapsulation of Heavy Metal Phosphate Nanophases in Vitreous Silica for Basic Research Studies and Nuclear Waste Storage

Metal-rich nanophases in vitreous silica with unusual optical properties are being created and investigated as a part of a fundamental effort to understand aggregation phenomena in our Office of Basic Energy Sciences work. These phases are also the basis for a novel nuclear waste form that is being developed in our Nuclear Energy Research Initiative program. The basis of these materials is a chemically functionalized, highly porous silica that is termed Diphosil. Chiarizia and coworkers created Diphosil as an ion exchange material that strongly and selectively sorbs highly charged metal ions, such as actinides, from acidic aqueous solutions [1]. Diphosphonic acid groups dispersed in Diphosil are responsible for the metal ion chelation.

Our research has shown that heating metal ion-loaded Diphosil in air at elevated temperatures oxidizes the functional groups thereby volatilizing the organic species and converting the phosphonic acid groups to phosphoric acid that will react with metal ions within the pores of the silica [2]. Further heating causes pore collapse that encapsulates and chemically fixes the metal ions, as phosphates, in vitreous silica. Our laser photophysics studies and small angle neutron scattering studies at IPNS provided clear evidence for the nanophase character of metal ion-loaded thermally densified Diphosil. Furthermore, the nanophases are inaccessible to water and their size is strongly dependent on the type of metal ion. These results have direct impact on development of Diphosil and related phases for nuclear waste treatment and subsequent storage.

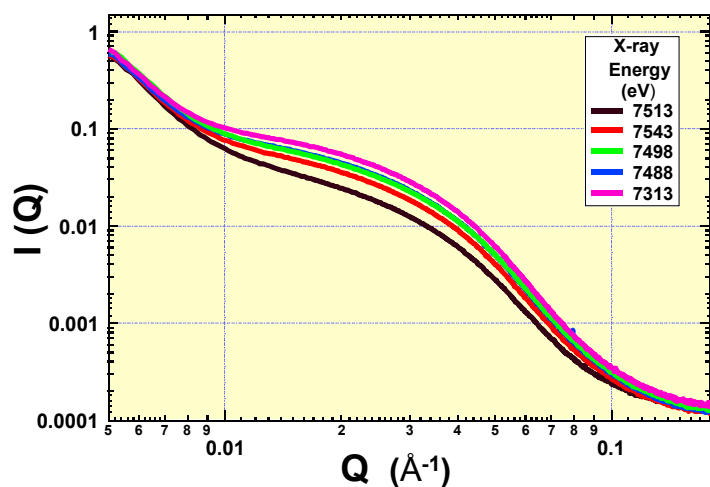


Figure 1. The monotonic decrease of $I(Q)$ as a function of energy of x-rays near the L_3 edge of Tb (7513 eV) for a Tb-loaded Diphosil sample clearly indicates the encapsulation of the Tb nanophases in silica.

We have also obtained direct evidence for the presence and size of heavy metal-containing nanophases in thermally densified, lanthanide ion-loaded Diphosil by using anomalous small angle x-ray scattering (ASAXS) at BESSRC-CAT at APS. An example of the ASAXS data is shown in Fig. 1 for the case of terbium (Tb)-loaded Diphosil that had been heated to 1100 °C. The monotonic decrease in intensity of scattered x-rays over a particular range of scattering vector, Q (where $Q = 4\pi\sin\theta/\lambda$ and λ is the incident x-ray wavelength), is indicative of Tb-containing nanophases whose size, if spherical, is 15.9 nm. These studies are providing

fundamental insight into pore collapse and subsequent aggregation and nanophase formation in heavy metal ion-loaded Diphosil that is undergoing thermal densification.

1. R. Chiarizia, E. P. Horwitz, K. A. D'Arcy, S. D. Alexandratos, and A. W. Trochimczuk, *Solvent Extraction and Ion Exchange*, **14**, 1077-1100 (1996).
2. J. V. Beitz and C. W. Williams, *Solvent Extraction and Ion Exchange*, **19**, 699-723 (2001).

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